

Sonochemistry under an Applied Magnetic Field: Determining the Shape of a Magnetic Particle

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The sonochemical irradiation of $\text{Fe}(\text{CO})_5$ solution in Decalin has been carried out with and without an external magnetic field. Direct TEM measurements reveal that the sample obtained without a magnetic field consists of spongelike particles with a mean size of about 25 nm, whereas the sample synthesized in a 7 kG magnetic field consists of highly acicular particles of 50 nm in length and 5 nm in width. Our finding sheds light on the process of particle nucleation during sonication, which cannot be a diffusion-assisted growth because of the very small time scale. We conclude, therefore, that particles are forced to form an acicular entity by direct magnetic interactions. The amorphous nature of the as-prepared substance was verified by X-ray diffraction, selected area electron diffraction, and differential scanning calorimetry. The magnetic moment vs temperature measurements and Mössbauer spectroscopy reveal a large shift of the blocking temperature of about 70 K toward higher temperatures for the sample obtained in magnetic field. We attribute the observed shift to the significant enhancement of the particle shape magnetic anisotropy.

Introduction

The pioneering work of Suslick and co-workers has demonstrated the possibility of synthesizing nanophased amorphous iron by passing ultrasound radiation through $\text{Fe}(\text{CO})_5$.^{1,2} This work has led to an extensive investigation of the decarbonylation reaction. Following Suslick's method, alloys,^{3–6} carbides,⁷ nitrides,⁸ oxides,^{9,10} and various ferrites¹¹ have also been prepared. In all cases, the products are obtained in the amorphous form, with the particles of nanometer size. Owing to the magnetic nature of the products, they are highly aggregated, which makes it difficult to detect the individual particles by using TEM. However, the agglomerates and the few separated particles are observed as rounded particles.

The particle shape can be determined by various methods, for example, by wet chemical techniques. The works of Pileni^{12,13} have shown the formation of elongated copper particles by the reduction of copper(II) in the presence of a cylindrical colloidal assembly. Nikles and co-workers^{14,15} reduced ferrous ions dissolved in water droplets with sodium borohydride in the presence of a magnetic field. They obtained acicular iron particles that contained, however, spherical particles and chains of spherical particles as well. In a later publication¹⁶ they embedded the ferrous ions in tubular lecithin assemblies and carried out the reduction in a magnetic field of 1.2 kG. The aliquots removed after 2 min contained more than 90% acicular iron particles.

We have recently reported on the synthesis of amorphous nanophased iron oxide via the sonication of iron pentacarbonyl under ambient atmosphere.⁹ In the current study, the same reaction was carried out while the sonication cell was placed between the poles of a magnetic field. The shapes of the iron oxide nanoparticles were different from those observed in the

absence of a magnetic field. This difference is also reflected in the magnetic properties as well as in the Mössbauer spectra of these particles.

Experimental Section

The process of regular sonochemical synthesis of amorphous iron oxide nanoparticles has been described elsewhere.⁹ Briefly, a 1 M solution of $\text{Fe}(\text{CO})_5$ in Decalin was sonochemically irradiated under ambient atmosphere for 3 h. Similarly, the sonochemical irradiation of 1 M solution of $\text{Fe}(\text{CO})_5$ in Decalin was performed in the presence of the applied external homogeneous magnetic field of 7 kG. In the both cases, the powder obtained was centrifuged, washed repeatedly with dry pentane (6–7 times, 8500 rpm), dried in a vacuum at room temperature for 3 h, and annealed in a vacuum at 140° C for 3 h in order to remove organic residua. The samples were then subjected to further analysis.

The powder X-ray diffraction measurements were performed on powder Rigaku X-ray diffractometer (Cu $K\alpha$ radiation, $\lambda = 0.15418$ nm).

The TEM study was performed using a JEOL Instruments JEM-1200EX electron microscope (JEM 1200EX-3). An amount of 0.2 mg of material was dispersed in 50 mL of pentane and stirred in the sonication bath for 10 min. A drop of suspension was placed on the carbon film supported by the copper grid, dried at room temperature for 15 min to evaporate the solvent, and subjected to TEM analysis.

The DSC measurements were carried out on a Mettler DSC-30 instrument (Mettler TC11 TA processor).

Mössbauer spectroscopy studies were carried out using a conventional constant acceleration spectrometer. The ^{57}Fe Mössbauer spectra (MS) were measured with a 50 mCi ^{57}Co :Rh source. The spectra at various temperatures were least-squares-fitted with one or two subspectra. The isomer shift (IS) values are relative to Fe metal at 300 K.

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Magnetic measurements were conducted using a Quantum Design MPMS SQUID (superconducting quantum interference device) magnetometer. First, the blocking temperature was measured by cooling the sample in zero field down to 5 K, at which point a magnetic field of 500 G was applied. After that, the sample was slowly warmed to a high temperature (typically 300 K) in steps of a few Kelvin, with stabilization at each temperature and subsequent measurements of the magnetic moment (this is the so-called zero-field cooled measurement (ZFC)). Then, without turning off the magnetic field, the sample was cooled to 5 K with measurements of the magnetic moment at each intermediate temperature (field-cooled measurements (FC)). The temperature at which the two curves ZFC and FC merge is traditionally called the blocking temperature T_B . This pretty well-defined temperature is the important parameter characterizing the magnetic behavior of ultrafine particles.

Results

Figure 1a and Figure 1b,c depict the TEM images of samples obtained using sonication with and without the applied magnetic field of 7 kG, respectively. There is an obvious difference not only in the particles' shape but also in their size. The estimated amount of acicular iron oxide nanoparticles is 20–30%. Usually, sonication yields amorphous nanostructures.^{1,3–5,9,17,18} Surprisingly enough, the acicular particles obtained in a magnetic field are also amorphous. This conclusion is based on results from XRD (X-ray diffraction), SAED (selected area electron diffraction), and DSC (differential scanning calorimetry) studies.

The results of the XRD analysis for both materials are presented in Figure 2. The absence of Bragg diffraction peaks suggests the absence of long-range crystalline order in the examined substance. These data are consistent with electron diffraction patterns (see insets to Figure 1).

Figure 3a presents the DSC spectrum of iron oxide prepared in the presence of an applied magnetic field of 7 kG. This spectrum is typical of a product obtained in the amorphous state^{9,10} (see Figure 3b). The strong exothermic peak, which appears at around 300° C, is due to the crystallization process, which implies that the as-prepared material is in the amorphous state. The slight difference in the heats of crystallization parts a and b of Figure 3 may be explained by the change of the particle's geometry. These data are consistent with the results from the XRD study and electron diffraction patterns (see Figure 2a and inset to Figure 1).

The room-temperature Mössbauer spectra (MS) of ^{57}Fe for both samples are displayed in Figure 4. The main information obtained from visual and computer analysis is the presence of only one broad doublet in both materials, indicating clearly that no long-range magnetic ordering is present. The hyperfine parameters for the regular amorphous Fe_2O_3 sample are isomer shift $\text{IS} = 0.48(1)$ and quadrupole splitting $\Delta = eqQ/2 = 0.91(1)$ with a line width of $0.56(1)$ mm/s. The hyperfine parameters for the sample, which consists of acicular iron oxide nanoparticles, are quite similar: $\text{IS} = 0.37(1)$ and $\Delta = 0.78$ mm/s. In other words, for these two iron oxide samples we detect similar MS, with only a difference in the broadness of the doublet line. For the case of acicular nanoparticles, the line width is somewhat broader, and we shall refer to this fact hereafter. These values are typical of Fe^{3+} ions in the high-spin state, and we attribute these doublets to the presence of Fe_2O_3 in the amorphous form. Note that similar values are obtained for the MS of the amorphous Fe_2O_3 ,¹⁹ which is consistent with our present interpretation.

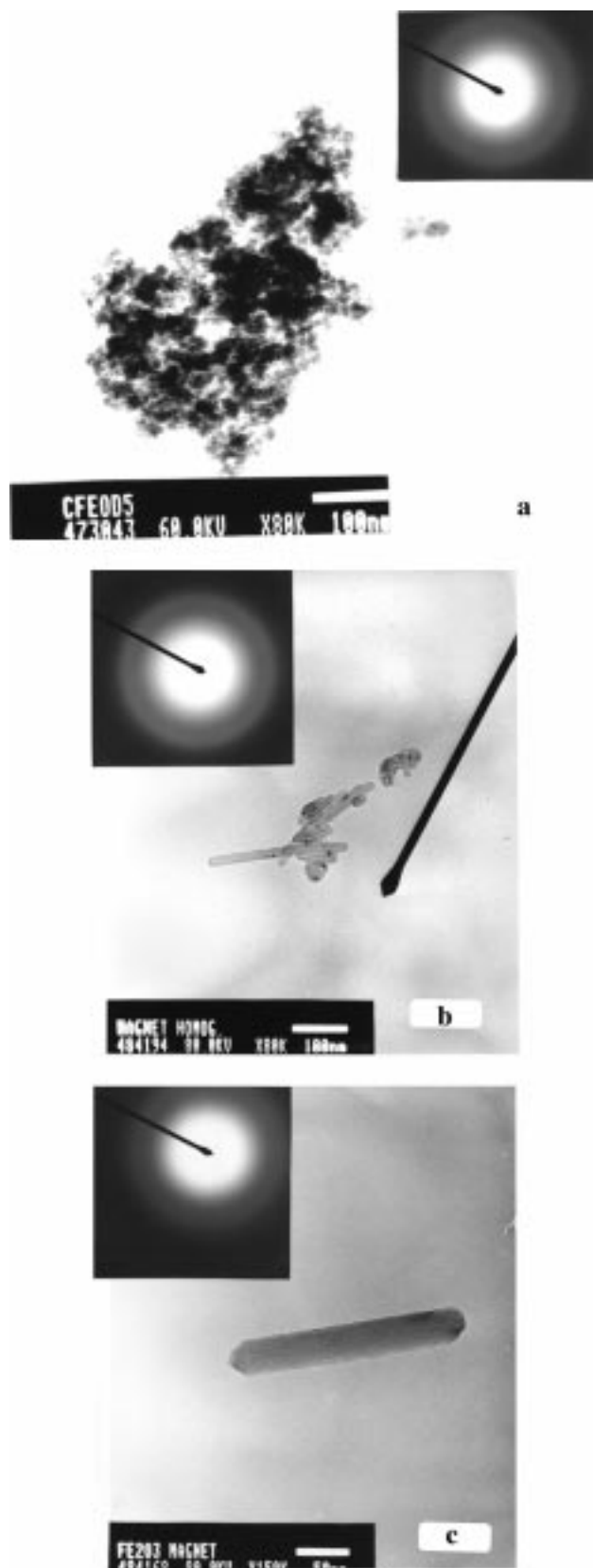


Figure 1. TEM images of amorphous iron oxide nanoparticles: (a) iron oxide synthesized using the regular sonication procedure; (a, inset) selected area electron diffraction pattern; (b, c) iron oxide prepared in the presence of applied magnetic field; (b and c insets) selected area electron diffraction patterns.

A different behavior is observed at 90 K. The results of Mössbauer spectroscopy show that in the sample synthesized without the magnetic field, the sextet, which indicate a magnetic

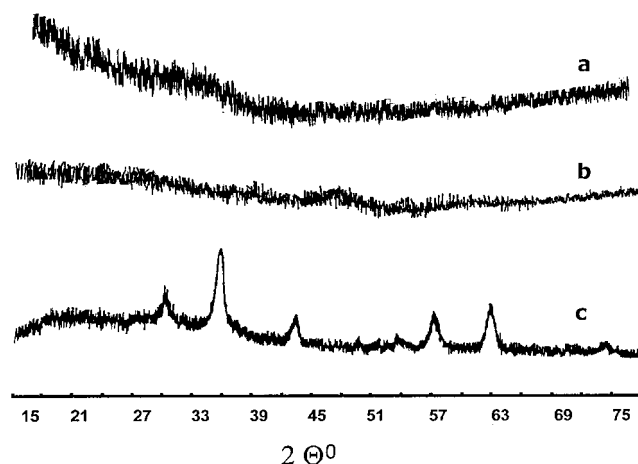


Figure 2. X-ray powder diffraction patterns of various iron oxide nanoparticles: (a) iron oxide prepared in the presence of an applied magnetic field; (b) iron oxide synthesized using the regular sonication procedure; (c) nanocrystalline γ - Fe_2O_3 .

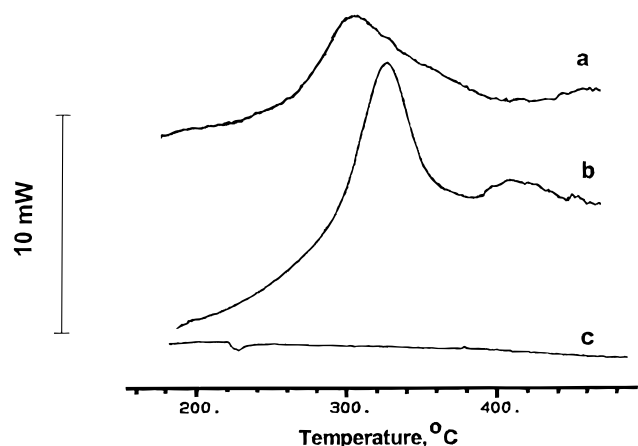


Figure 3. DSC spectra of different iron oxides: (a) amorphous iron oxide prepared in the presence of an applied magnetic field of 7 kG; (b) typical spectrum for amorphous iron oxide prepared using the regular sonication procedure; (c) nanocrystalline γ - Fe_2O_3 .

ordered structure, disappears at about 90 K (see Figure 5a). Above this temperature, the Mössbauer spectrum may be well-described by a doublet, which is characteristic of a paramagnetic structure. Here, the transition from the superparamagnetic (i.e., ferromagnetic) to the paramagnetic state is abrupt. Figure 5a shows a broad doublet for the sample synthesized without the magnetic field, whereas for material prepared in the presence of an applied magnetic field, the spectrum clearly shows a hyperfine magnetic splitting. This result is evidence of long-range magnetic ordering at low temperatures. The fit of the doublet yields $\text{IS} = 0.49(1)$ and $\Delta = 1.01(1)$ mm/s with a line width of 0.85 mm/s. The broadening of the line width (here, $T_B < 90$ K) may be a result of some short-range magnetic interactions very close to T_B . The major problem confronting any quantitative analysis of the magnetic spectrum is the amorphous nature of the materials, which induces uniform magnetic hyperfine field at the ^{57}Fe nuclei. Therefore, to fit the Mössbauer spectrum at 90 K, a distribution of magnetic hyperfine fields was used. The IS and line width values obtained are $\text{IS} = 0.45(1)$ and 0.59 mm/s, with an average hyperfine field of $H_{\text{eff}} = 523(2)$ kOe. The spectra obtained at 110 and 130 K (not shown) are analogous to the 90 K spectrum (Figure 5b), with similar hyperfine parameters. We are aware that these values are not conclusive, and by use of alternative initial values, different hyperfine parameters can be obtained.

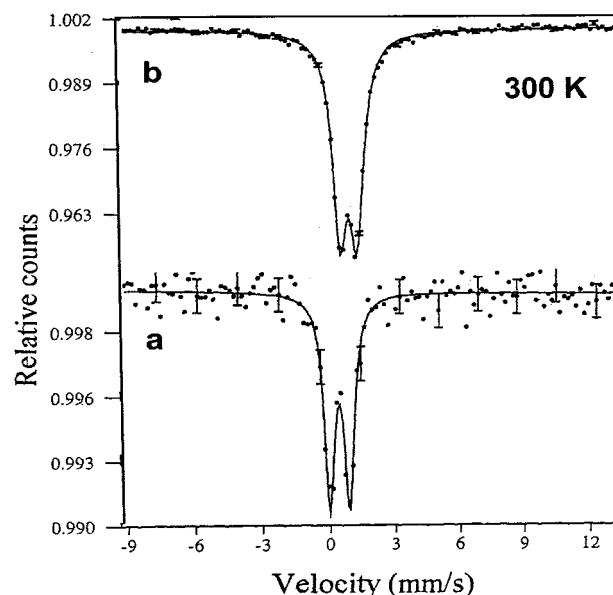


Figure 4. Mössbauer spectra of amorphous iron oxides at 300 K: (a) iron oxide prepared using the regular sonication procedure; (b) iron oxide prepared in the presence of an applied magnetic field of 7 kG.

However, the H_{eff} value obtained below the blocking temperature (at 90–130 K) is in perfect agreement with the reported value of γ - Fe_2O_3 ($H_{\text{eff}} = 520$ kOe).²⁰ The same H_{eff} value is obtained at 100 and 130 K. This indicates that the hyperfine field on the Fe nuclei is the same, regardless of whether the iron oxide is amorphous or crystalline.

The material prepared in the presence of an applied magnetic field behaves differently (see Figure 5b). The main effect detected in Figure 5 is that as the temperature is raised, the magnetic splitting decreases and a paramagnetic doublet in the central part of the spectrum is observed. The hyperfine parameters for this doublet are similar (within experimental error) to those obtained at 300 K (see above). The relative ratios of the magnetic subspectra decrease with temperature: 65% and 33% at 150 and 180 K, respectively. Even at 240 K (well above the blocking temperature), about 12% of the magnetic subspectra are still observed. The average H_{eff} values obtained at 150, 180, 200, and 240 K are 390(5), 382(5), 249(1), and 218(20) kOe, respectively. Above 240 K the spectra are well fitted with a pure doublet, but the existence of a small fraction of magnetic splitting cannot be excluded.

The field distribution, in particular, the smeared spectra and the paramagnetic doublet obtained above 130 K, is obviously due to a distribution in T_B ($\Delta T_B > 100$ K) resulting from some inhomogeneity in the particle sizes throughout the amorphous material. The “traces” of sextet are observed up to almost 240 K, and the transition from the sextet to doublet is gradual. The paramagnetic phase appears first at 130–135 K (T_B , determined using magnetic measurements, is shown below) and gradually increases, reaching 100% at about 240 K. We assume that T_B of the sample, which consists of acicular nanoparticles, depends on the particle’s size, and, therefore, the disappearance of the magnetic subspectrum is also temperature dependent.

We have also conducted measurements of magnetic moment as a function of temperature. The results are shown in Figure 6. Below the blocking temperature T_B , ZFC and FC curves do not coincide. Above T_B , both materials exhibit superparamagnetic behavior. However, the blocking temperature of the sample obtained without a magnetic field ($T_B \approx 80$ K) is approximately 70 K lower than that of the sample synthesized

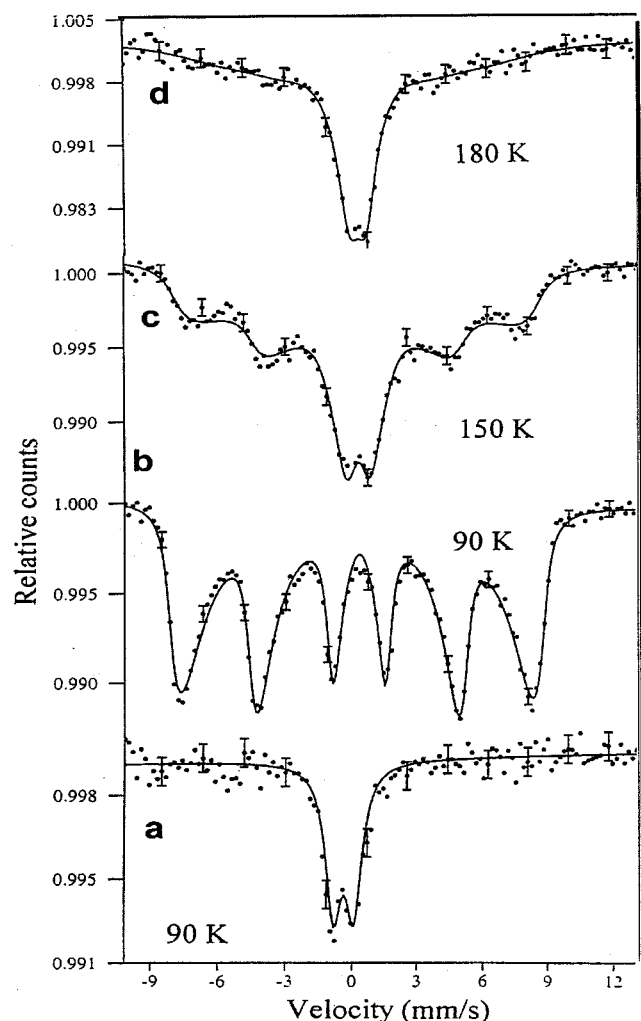


Figure 5. Mössbauer spectra of amorphous iron oxides taken at various temperatures: (a) iron oxide prepared using the regular sonication procedure; (b–d) iron oxide prepared in the presence of an applied magnetic field of 7 kG.

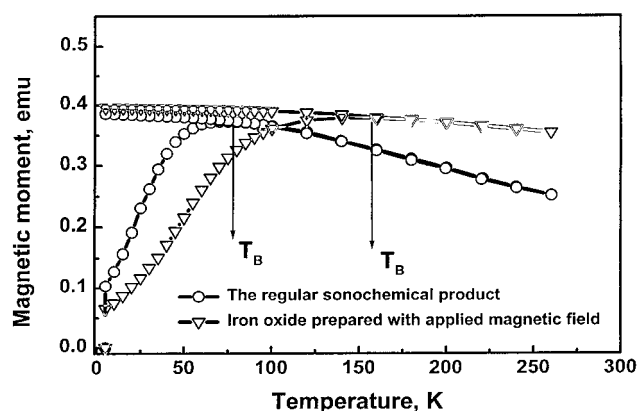


Figure 6. Magnetic moment vs temperature measurements. There is a shift of T_B toward the higher temperatures attributed to the nanoparticles' shape anisotropies.

in the presence of a magnetic field ($T_B \approx 150$ K). We interpret this shift in terms of magnetic shape anisotropy, which is significantly enhanced in the case of the acicular nanoparticles.

The influence of the magnetic field on the growth of ferromagnetic particles is known. In most of the cases, particle growth is a diffusion-assisted slow process. In such cases, the magnetic field determines the preferable direction for the

magnetic atoms motion, hence assisting the growth in that direction. Typical time of such experiments is 10–100 s.

In contrast, in the present work the sonochemical method has a very short characteristic time with respect to the particle growth, i.e., the collapse of the cavity is estimated to occur in less than a nanosecond.^{18,21,22} In this case, the formation of acicular particles can be explained by considering the direct magnetic interactions between particles.

Conclusions

In conclusion, in this work we have demonstrated, for the first time, the synthesis of amorphous elongated iron oxide nanoparticles by using ultrasound radiation in the presence of a magnetic field. This allows the control of the magnetic shape anisotropy. The results might be of importance to the improvement of the materials used for magnetic storage. The current results will be of interest to scientists in the fields of physics of nanoparticles on one hand and to physical chemists involved with particle growth in the presence of a magnetic field on the other.

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